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Flexible CZTS Thin Film Solar Cells Prepared and Fabricated by Spray Deposition Method

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ABSTRACT

Cu_2ZnSnS_4 (CZTS) thin films on flexible substrates have been prepared by Spray Pyrolysis deposition method. Toxic free and inexpensive CZTS thin films are very promising potential candidate for high efficiency green energy production. The CZTS film elements using precursor spray solution with thiourea, copper chloride, zinc chloride, and tin chloride in different concentration ratios onto flexible Al-foil substrate at ambient conditions. The deposited films were subjected to X-ray diffraction (XRD), Scanning electron microscopy (SEM) and UV-Vis measurements. The grain size, crystallite structure and lattice parameters are taken from X-ray diffraction (XRD). Thickness of the film and defects are done from Scanning electron microscopy (SEM) analysis. UV-Vis study showed high optical absorption coefficient and wide direct band gap for solar region. The structure of CZTS solar cells on the form of **Al-foil/Mo/CZTS/i-ZnO/ITO/Al-Ni**, grid was tentatively fabricated. The best solar cell showed a short-circuit current density (I_{sc}), open-circuit voltage (V_{oc}), a fill factor (FF) and efficiency under AM 1.5(100mW/Cm^2) illumination. These results demonstrate the CZTS thin films were successfully deposited by low cost Spray Pyrolysis deposition method.

Keywords: Flexible substrates, Spray, grain size, CZTS, direct band gap, efficiency.

1. INTRODUCTION

Chalcogenide based thin film materials like CZTS with higher absorption coefficient have been strongly suitable for the cost effective and environmental-friendly approach because they are earth abundant constituent materials such as Zn and Sn are cheap, non-toxic[1] and readily available materials for PV applications in nature[2]. Spray pyrolysis through is expensive, requires the use of sophisticated materials and overall, it is not impressive, now good quality semiconductors which allows fabrication of solar cells with satisfactory efficiency.

Cu_2ZnSnS_4 thin films have received considerable attention due to their applications in thin film solar cells. One of the most promising techniques for producing large areas of inexpensive CZTS thin film for terrestrial photovoltaic application is spray pyrolysis and here we followed this method to synthesize the CZTS film on flexible substrates.

2. EXPERIMENTAL DETAILS

Thin films of CZTS were obtained using the spray pyrolysis deposition technique (SPD) from an aqueous solution. Copper dichloride dehydrate, Zinc acetate, tin chloride and thiourea (CH_4N_2S) were used as Copper, Zinc, Tin and Sulfur precursors. Solutions with different molar ratio were prepared: 0.01M: 0.005M: 0.005M: 0.04M using deionized water. Using a hot plate the substrates were heated at the deposition temperature. The deposition parameters such as the spraying distance from the nozzle to the substrate and the carrier gas pressure were set at previously optimized values[3]. Thus, the spraying distance was 20 cm and was kept constant for all depositions. The temperature, the number of sprayed sequences and the Cu: Zn: Sn: S ratios were the three variables investigated in this study. Temperature was invariant at 300^{o}C. Film obtained after 15 spraying sequences, with 3 layers were obtained.

The as-deposited films were characterized using X-ray diffraction using an Advanced Rigaku diffractometer; the film thickness and energy band gap were measured from the UV-Visible absorption spectra using a Perkin Elmer Lambda 25 photo spectrometer.

3. RESULTS AND DISCUSSION

3.1 XRD analysis

The structural analysis of CZTS thin films was carried out by using X-ray diffractometer. The X-ray diffraction patterns of the CZTS thin films, on glass substrates are shown in Figure 1.The XRD analysis shows that the thin films are kesterite phase CZTS with lattice parameters a = 5.3928Å and c = 10.746Å which is almost in agreement with the standard data from JCPDS card No 21-0883. There is no difference among the XRD patterns of the nano-materials. The planes are oriented in the direction (112), (103), (004), (211) and (114). The films exhibit tetragonal crystal structure. The highest intensity peak corresponds to (112) preferred orientation. The (112) peak is stronger than other peaks. In general, the preferential orientation of the films is along the (112) direction.

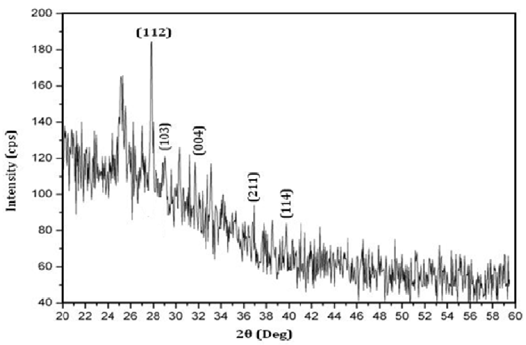


Fig.1 XRD pattern spectrum of the Cu_2ZnSnS_4 film

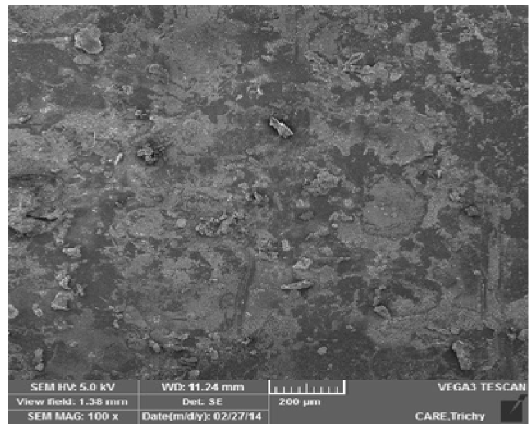
More importantly none of these peaks belong to CZTS compound. Using Debye Scherrer's formula crystallite sizes were calculated from the XRD spectrum of powder sample and found to be 3-7nm. Debye Scherrer's formula is expressed as

$$D = \frac{0.98\,\lambda}{\beta Cos\,\theta} \qquad (1)$$

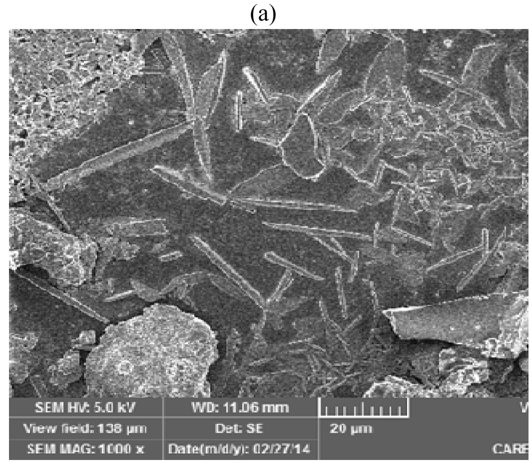
Where D is the crystalline size, k is the wavelength of the X-ray radiation used, β is the full width at half maximum (FWHM) of the diffraction peak and h is the Bragg diffraction angle of the XRD peak[4].

3.2 Morphological analysis

Fig.2 (a-b) shows the SEM images of the Cu_2ZnSnS_4 film. From Fig.2, it can be seen that a large amount of micro grains exist on the glass. After the annealing, although the surface morphology is still coarse, large agglomeration of grains and few voids in the film are observed, which is beneficial in photovoltaic application. In addition, we also see that the grains are covered with cluster. The corresponding mechanics should be further analyzed.



(a)



(b)

Figure 2: The SEM images of the CZTS thin film (a) 200 µm (b) 20 µm

Due to volume contraction arising from the evaporation of volatile products, cracks exist in the film. Organic binders in the CZTS precursor sol-gel could prevent the formation of cracks[5]. High temperature annealing could improve the crystallinity and increase the grain size of thin films[6].

3.3 Optical Properties

The optical absorption coefficient versus the photo energy of the Cu_2ZnSnS_4

film seen that the annealed film has a large optical absorption coefficient, which is larger than $10^4 cm^{-1}$ in the visible wavelength region indicating the value is suitable for solar cell applications of thin films. The optical band gap energy of the Cu_2ZnSnS_4 film can be estimated from the $(\alpha h\nu)^2$ versus $h\nu$ graph by extrapolating the linear absorption edge part of the curve. The result shows that the optical band gap of the Cu_2ZnSnS_4 film is around 1.5eV achieved[7].

4. CHARACTERIZATION OF THE CELL

For the spray deposited CZTS material, the power conversion efficiency (η) of the device was relatively low (1.02%), since the data of photovoltaic parameters such as Jsc, Voc, and FF were low.

5. CONCLUSIONS

In this work, we used the kesterite CZTS thin films on flexible substrates as effective Conversion efficiencies in solar cells. The structure of CZTS solar cells on the form of Al-foil/Mo/CZTS/i-ZnO/ITO/Al-Ni, grid was tentatively fabricated. The best solar cell showed a short-circuit current density (I_{sc}), open-circuit voltage (V_{oc}), a fill factor (FF) and efficiency under AM 1.5 ($100mW/Cm^2$) illumination. These results demonstrate the CZTS thin films were successfully deposited by low cost Spray Pyrolysis deposition method. The measurement of the photovoltaic performance of spray deposited kesterite CZTS exhibited solar energy conversion efficiency (1.02%). The excellent performance of the CZTS thin films paves a new pathway for preparing cheap and highly efficient solar cells on flexible substrates.

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